

mixture, usually by filtration. The separated coated pigment particles, obtained, for example, as a presscake, may be dried by heating to form a powder. Preferably a solution of the polymer in water, a water-miscible organic solvent or a mixture thereof is mixed with an aqueous dispersion of the pigment. The pigment dispersion is conveniently formed by redispersing a pigment presscake in water or a mixture of water with a minor amount of a water-miscible organic solvent. The mixture of pigment dispersion and polymer or polymer solution may be heated, if desired. Optimum conditions, such as temperature and stirring times, for particular pigments and coating polymers can readily be determined by simple experiment.

The formation of the polymer coating on the pigment particles may be as a result of adsorption of the polymer on the surface of the pigment. Where the polymer is in solution in an organic solvent, it may be helpful to add water to facilitate adsorption of the polymer on the pigment. If desired the polymer may be precipitated from a solution thereof onto the pigment particles by addition of a precipitant salt such as sodium chloride or sodium sulphate to the mixture of the pigment dispersion and the polymer solution.

The vinyl or cellulosic polymer is generally used in an amount of 0.1 to 20%, preferably 1 to 15%, by weight, of the pigment.

The coating of the vinyl or cellulosic polymer on the pigment particles may be crosslinked by treatment of the polymer with a crosslinking agent therefor. This treatment is conveniently carried out in the liquid medium in which coating of the pigment particles is effected before separation of the coated particles from the medium, although it could be carried out by treating the coated pigment particles with the crosslinking agent after such separation, for example in another solvent or mixture of solvents.

Suitable crosslinking agents include boron oxyacids and their salts, for example boric acids such as orthoboric acid, metaboric acid and polyboric acids and their salts, usually alkali metal salts, and boronic acids, usually akaneboronic acids such as methaneboronic and ethaneboronic acids or arylboronic acids such as phenylboronic acid, and their salts; phosphoric acids, such as orthophosphoric acid, and their salts, usually alkali metal salts; aliphatic and aromatic aldehydes such as formaldehyde, acetaldehyde, propionaldehyde, n-butyraldehyde, isobutyraldehyde, n-valeraldehyde, n-caproaldehyde, n-heptaldehyde, glyoxal, succinic dialdehyde, glutaric dialdehyde, adipic dialdehyde and benzaldehyde; carboxylic acids and their halides or salts, usually di(acid halides) of dicarboxylic acids such as oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, tetrahydrophthalic acid, hexahydrophthalic acid and phthalic acid; alkylene dihalides, usually C<sub>1</sub> to C<sub>6</sub> alkylene dihalides such as methylene-, ethylene-, ethylidene-, trimethylene-, tetramethylene-, pentamethylene- and hexamethylene dihalides, usually dibromides or, preferably, dichlorides; aluminium salts such as aluminium nitrate, aluminium sulphate, sodium aluminium sulphate or potassium aluminium sulphate; zinc compounds, including salts and complexes such as zinc chloride, zinc acetate, zinc benzoate, zinc glycinate, zinc alaninate, zinc ammonium bicarbonate or zinc ammonium glycinate; and polyisocyanates, usually diisocyanates such as 1, 2-propylene-, 1,4-butylene-, pentamethylene-, hexamethylene-, dodecamethylene-, 1,4-cyclohexylene-, and methyl-2, 4-cyclohexylene diisocyanates, 3-isocyanatomethyl-3, 5,5-trimethylcyclohexyl isocyanate (isophorone diisocyanate), 2,4- and 2,6-tolylene diisocyanates and 4,4'-diphenylmethanediisocyanate.

Other suitable crosslinking agents are akoxides of elements of Group IVA or Group IVB of the Periodic Table, usually having at least two alkoxy groups per molecule, trialkoxides and tetra-alkoxides being preferred. The akoxides are usually those of tin, lead, germanium or, preferably, of silicon, titanium or zirconium. The alkoxide groups preferably each have from 1 to 4 carbon atoms, as in sec-butoxide or tert-butoxide groups or, especially, methoxide, ethoxide, n-propoxide, isopropoxide or n-butoxide groups.

Further suitable crosslinking agents are inorganic silicon (IV), tin (IV), titanium (IV) and zirconium (IV) compounds, including silicates which form active silica on hydrolysis, e.g. as described in US Patents 3370971 and 3639133, such as silicic acid, metasilicates or sodium silicate, tin (IV) chloride, titanium (IV) oxysulphate, zirconium (IV) acetate, zirconium (IV) nitrate, also known as zirconyl nitrate, zirconium (IV) oxychloride (ZrOCl<sub>2</sub>) and zirconium (IV) orthosulphate, also known as zirconyl sulphate; and aluminates which form alumina on hydrolysis, including water-soluble aluminates such as sodium, potassium and magnesium aluminates.

It will be apparent that choice of the crosslinking agent for a particular coating polymer will depend on the nature of the reactive groups present in that polymer. For example, many of the abovementioned crosslinking agents can be used to crosslink hydroxyl- or carboxyl-containing polymers, whereas some of these agents are used normally with hydroxyl- containing polymers and others are used normally with carboxyl-containing polymers.

Preferred crosslinking agents, particularly for use with hydroxyl-containing polymers, include boric acids and their salts, preferably sodium and potassium salts, especially orthoboric acid and sodium tetraborate; phosphoric acids and their salts, preferably sodium and potassium salts, especially sodium orthophosphate; silicon (IV) trialkoxides or tetra-alkoxides, preferably trialkoxysilyl-substituted C<sub>1</sub> to C<sub>6</sub> alkyl esters of acrylic or methacrylic acid, especially 3-(trimethoxysilyl)propyl methacrylate; silicates which form active silica on hy-



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(54) **Method of improving storage stability of pigments.**

(57) A method of improving the storage stability of a coloured organic pigment in powder form which comprises coating pigment particles with a solid polymer which is a polar group - containing vinyl polymer, said polar group being a hydroxy, carboxyl, carboxylic ester, anhydride or carboxamide group, or a cellulosic polymer, thereby inhibiting reduction of tinting strength of the pigment on storage.

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Red 3, Red 12 and, especially, Orange 5. The invention is also particularly useful where the pigment is a basic dye complex such as C.I. Pigment Violet 3.

Various co-additives may be used together with a pigment treated according to the invention in pigment compositions. Examples of such co-additives, which are generally used in a total amount of 1 to 50% by weight of the total pigment composition, include surfactants, resins and long chain fatty acids and amines. Surfactants used may be of the anionic type, such as fatty acid taurides, fatty acid N-methyltaurides, fatty acid isothionates, alkylbenzenesulphonates, alkyl naphthalenesulphonates, alkylphenol polyglycol ether sulphates and fatty alcohol polyglycol ether sulphates; fatty acids, such as palmitic, stearic and oleic acids; soaps such as alkali metal salts of fatty acids and naphthenic acids; cationic surfactants include quaternary ammonium salts, and N-oxides of tertiary amines or salts thereof; non-ionic surfactants include fatty alcohol polyglycol ethers (ethoxylated fatty alcohols), fatty acid polyglycol esters, alkylphenol polyglycol ethers and dialkyl polyglycol ethers. Resins include wood rosin, hydrogenated wood rosin, and polyamide resins e.g. those produced by condensing phthalic anhydride with long chain amines. Amines which may be added include long chain primary amines e.g. stearylamine; amine derivatives of wood rosin; N-long chain alkylalkylene diamines; polyamines; beta-amines, polyamide/polyamine derivatives of ethoxylated fatty amines and diamines, and derivatives of these compounds.

The present invention also provides a high molecular weight material pigmented with a pigment treated by the method of the invention as hereinbefore described, including high molecular weight material pigmented with the novel particulate compositions as hereinbefore defined. High molecular weight materials which may be pigmented with a pigment treated in accordance with the invention include cellulose ethers and esters such as ethylcellulose, nitrocellulose, cellulose acetate, cellulose butyrate, aminoplasts such as urea-formaldehyde and melamine-formaldehyde resins, alkyd resins, phenoplasts, polycarbonates, polyolefines, polystyrenes, polyvinyl chlorides, polyamides, polyurethanes, polyesters, rubbers, casein and silicones. These high molecular weight materials may be in the form of solids or liquids or in solution, for example in spinning solutions, varnishes, paints and printing inks. The coated pigments produced by the method of the invention are generally incorporated in an amount of 0.01 to 30%, preferably 0.1 to 15%, by weight of the high molecular weight material.

The improved storage stability which can be achieved by the present invention is particularly useful for pigments to be used with high molecular weight materials such as alkyd resins in surface coating compositions such as paints or printing inks.

The invention is illustrated by the following Examples, in which parts and percentages are by weight unless otherwise indicated.

#### Example 1

C.I. Pigment Yellow 74 aqueous presscake (33% solids) (182g) is re-dispersed in 600 ml water in a conventional manner. To the resulting aqueous suspension at room temperature is added a solution of a polyvinylalcohol having a number average molecular weight of 14,000 (6.1g, 10% on pigment weight) dissolved in water (300 ml). The mixture is stirred for 2.5 hours. A solution of boric acid (1.71 g, 0.2 mol per mol of vinyl alcohol) dissolved in water (60 ml) is added. The temperature is raised to 80°C and the pH increased to 8.1 by addition of dilute aqueous sodium hydroxide. The mixture is stirred for 1 hour at 80°C. After cooling to 70°C, the product is isolated by filtration, washed with water and kept as presscake. The presscake is dried at 65°C in an oven just prior to testing. The product thus obtained is found to have improved powder storage stability compared with the untreated pigment (see Table 1).

#### Example 2

CI Pigment Yellow 74 aqueous presscake (33% solids) (60g) is re-dispersed in 100g of a 2% solution of ethylcellulose in isopropanol (10% ethylcellulose on pigment weight). Isopropanol (150 ml) is added and the mixture is stirred for 85 minutes. Water (250 ml) is then added over 75 minutes at room temperature. A solution of sodium tetraborate (0.33g, 0.2 mol per mol of ethylcellulose) in water (20 ml) is added. The temperature is raised to 70°C and the pH increased to 7.8 by addition of dilute aqueous sodium hydroxide. The mixture is stirred for 1 hour at 70°C. The product is isolated by filtration, washed with water and kept as presscake. The presscake is dried at 65°C just prior to testing. The product thus obtained is found to have improved powder storage stability compared with the untreated pigment.

ber average molecular weight of 18,000 (4.2g) in water (50g) and the mixture is stirred and boiled at 99°C for 15 mins. A solution of sodium orthophosphate (1.4g) in water (50g) is added and the pH of the mixture is adjusted to 8.0 with dilute aqueous sodium hydroxide. The mixture is boiled at 99°C for a further 15 mins and then cooled at 70°C. The coated pigment is isolated by filtration, washed with water and dried at 70°C. The dried product is sieved, tested and found to have improved powder storage stability (see Table 4).

#### Example 9

CI Pigment Yellow 74 aqueous presscake (26% solids) (270g) is redispersed in water (500ml) in a conventional manner. To the aqueous suspension obtained is added a solution of Zinpol 1519 - 40% - W/IPA (10.5g) in water (50g) and the mixture is stirred and boiled at 99°C for 15 mins and then cooled to 70°C. The coated pigment is isolated by filtration, washed with water and dried at 70°C. The dried product is sieved, tested and found to have improved powder storage stability (see Table 4).

#### Example 10

To CI Pigment Yellow 74 aqueous slurry (5% pigment) (350g) is added a solution of a polyvinyl alcohol having a number average molecular weight of 18,000 (17.5g) in water (100ml). The slurry is heated at 99°C for 2 hours. A solution of zirconium acetate (32g of a 22%  $ZrO_2$  solution) in water is added and heating continued for 5 mins. The coated pigment is isolated by filtration, washed with water and dried at 68°C in an oven. The dried product is sieved and tested and found to have improved powder storage stability compared with the untreated pigment (see Table 5).

#### Examples 11 to 19

To determine the powder storage stability of pigments treated by the method of the invention, as well as the corresponding untreated pigment, the dried pigments are incorporated in a conventional manner into an alkyd paint system (SORBAL P470, an alkyd resin ex DSM Resins Ltd having a solids content 70%, white spirit, pigment; and driers solution).

	<u>MILLBASE</u>	<u>FINAL PAINT</u>
PIGMENTATION	20%	10%
PIGMENT/BINDER	1/1.4	1/4.7
SOLIDS CONTENT	35%	54%

The dried powders are each divided into two portions. One portion is tested in the above paint system immediately after drying. The other portion is stored at 40°C for 1 month before the paint is prepared.

The tinting strengths are assessed visually and instrumentally using datacolour DC-3890.

The results are given in Tables 1 to 5. The values correspond to the parts of pigment required to give an equal tinting strength to a defined standard. Lower values denote higher tinting strengths.

Table 4

	<u>Example</u>	<u>Pigment</u>	<u>Amount of Pigment Required</u>		<u>Loss of Strength</u>
			<u>Initial</u>	<u>1 month</u>	
5					
10	Control	CI Pigment Yellow 74	80	95	15
15	16	Example 7	125	130	5
	17	Example 8	80	85	5
20	18	Example 9	120	120	0
25					

Table 5

	<u>Example</u>	<u>Pigment</u>	<u>Amount of Pigment Required</u>		<u>Loss of Strength</u>
			<u>Initial</u>	<u>1 month</u>	
30					
35	Control	CI Pigment Yellow 74	107	125	18
40	19	Example 10	93	95	2

45 **Claims**

1. A method of improving the storage stability of a coloured organic pigment in powder form which comprises coating pigment particles with a solid polymer which is a polar group - containing vinyl polymer, said polar group being a hydroxy, carboxyl, carboxylic ester, anhydride or carboxamide group, or a cellulosic polymer, thereby inhibiting reduction of tinting strength of the pigment on storage.
2. A method according to claim 1, in which the polymer is a polyhydroxy vinyl polymer, a polycarboxy vinyl polymer, a N-vinyl pyrrolidone polymer or a cellulose ether.
3. A method according to claim 2, in which the polymer is a polyvinyl alcohol, a polyacrylic acid, a homopolymer of N-vinyl-2-pyrrolidone, or ethylcellulose.
4. A method according to any of claims 1 to 3, in which the solid polymer, or a solution or dispersion thereof



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# EUROPEAN SEARCH REPORT

Application Number

EP 92 30 7235

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 296 107 (CIBA-GEIGY AG)	1-10, 13, 14	C09B67/08
D	* the whole document * & US-A-4 889 562		
X	EP-A-0 296 106 (CIBA-GEIGY)	1-10, 13, 14	
P, X	* the whole document * EP-A-0 466 646 (CIBA-GEIGY AG) * page 3, line 14 - line 51; examples 7, 18 * claims 1, 2, 16 *	1-15	
A	EP-A-0 242 754 (BASF AG) * column 1, line 1 - column 3, line 40; examples *	1-5	
A	EP-A-0 022 746 (SANDOZ) * the whole document *	1-5	
A	EP-A-0 323 407 (CIBA-GEIGY) * example 5 *	1	
A	DE-B-1 270 208 (GENERAL ANILINE AND FILM CORP.) * column 2, line 45 - column 3, line 11; examples *	1	
A	US-A-3 904 562 (HOPFENBERG ET. AL.) * the whole document *	1	C09B C09D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 08 DECEMBER 1992	Examiner KETTERER M.
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons &amp; : member of the same patent family, corresponding document</p>			

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